Вісник ХНУ імені В.Н. Каразіна, серія «Фізика», вип. 37, р. 25-30 (2022)
The Journal of V.N. Karazìn Kharkiv National University. Series "Physics" Iss. 38, p. 25-30 (2023)
DOI: 10.26565/2222-5617-2023-38 ISSN 2222-5617 (Print)

Original article
In print article
https://doi.org/10.26565/2222-5617-2023-38-04
UDC 538.975
PACS numbers: 68.35.bd

MORPHOLOGICAL STRUCTURE OF THE PB ISLAND FILMS MELTED ON THE TA LAYER SURFACE

I.G. Churilov, O.O. Nevgasimov, S.I. Petrushenko, S.V. Dukarov, V.M. Sukhov

V.N. Karazin Kharkiv NationalUniversity, 4 Svoboda Sq., 61022 Kharkiv, Ukraine
E-mail: igor.churilov@karazin.ua

Received on April 05, 2023. Reviewed on May 11, 2023.
Accepted for publication on May 17, 2023.

An effective way to create self-organizing arrays of metal particles is to melt thin layers of substance on a poorly wetted surface. Such arrays may improve the technological properties of functional structures, and are themselves functional elements of modern devices and systems.

During the melting of a solid layer on a poorly wetted substrate, an array of spherical particles is formed, which are evenly distributed over the surface of the substrate. The distribution of particles by size is determined by the thickness of the fusible layer and conditions of the deposition. The location of islands, formed after the melting of vapour-crystal deposited solid films, is determined primarily by the initial stages of de-wetting, when the thin continuous film starts to decay while remaining in solid state.

This work studied self-organizing processes during the melting of Pb films deposited on a Ta substrate. The films were deposited on glass plates in a high vacuum and then after deposition were heated to a temperature slightly above the Pb melting point. After the heat treatment the samples were removed from the vacuum chamber and examined using SEM microscopy and EDS analysis.

It was discovered that arrays of spherical particles are formed during the melting of micron-thick Pb films. The histograms of the size distribution of such particles are quite wide and can be represented as bimodal with partially overlapping maxima. This can be explained by active coalescence processes in thicker samples. This study demonstrated that small temperature gradients can cause noticeable kinetic effects that allow separate particles to move macroscopic distances and capture the surrounding substance. The study also estimated the energy associated with the optimization of the morphological structure of vacuum condensate and which is a physical factor of de-wetting.

Keywords: *de-wetting, self-organization, island films, melting, particle arrays, size distribution*.

In cites: *I.G. Churilov, O.O. Nevgasimov, S.I. Petrushenko, S.V. Dukarov, V.M. Sukhov. Morphological structure of the Pb island films melted on the Ta layer surface*. The journal of V.N. Karazìn Kharkiv National University. Series "Physics" Iss. 38, 2023; 25-30. https://doi.org/10.26565/2222-5617-2023-38-04

INTRODUCTION

Arrays of metal particles, chemical compound particles, composites and organic particles are critically important for modern technologies, such as catalysis, green energy, medicine, etc. [1, 2, 3, 4]. Such arrays can be produced in different ways [5, 6, 7, 8, 9]. Vacuum thermal de-wetting of initially continuous films is a convenient method for research purposes [10, 11, 12, 13, 14, 15]. This method of nanoarray formation allows us to find out the fundamental patterns of self -organization of the film substance, that affect the technological features of the production of functional layers.

Previous studies of the processes of self-organization of substance of films under the temperature factor are presented in [16, 17, 18]. Studies have shown that an array of metal particles of a regular shape (a spherical segment) is formed during the melting of metal films on a carbon substrate. The formation of the spherical particles arrays has been observed during the melting of binary alloys [17]. At the same time, for metal-metal systems that have stronger interaction, significant differences from metal-nonmetal systems [16, 18] are expected. In the study of supercooling during crystallization of the Ag/Bi system [19], it was found that in the case of Bi condensation on Ag by the vapor-crystal mechanism, a connected system of bismuth inclusions of irregular shape is formed, which is not destroyed after cycles of melting and crystallization. The arrays of particles formed during the melting of the Pb-In alloy on a molybdenum substrate are separate particles of regular shape and are similar to those observed during the dispersion of metallic films on amorphous carbon. The structures formed during the melting of bismuth on a vanadium layer intermediate between these structures [20]. In this case, arrays of large separated particles are formed, which do not form a bonded system. Such contact pairs, which have an intermediate interaction between low-melting and higher-melting point components, are promising objects for research. In addition, layers of refractory materials that allow forming ultrathin electrically continuous films [21, 22, 23, 24, 25], are of interest to applied researchers for modern nanoelectronics.

Note, that the formation of self-organized arrays is a result of several simultaneous processes of decay, complicated by a possible coalescence of particles. Although the contribution of the coalescence process decreases with sample thickness, this process can have a significant impact on the formation of structures, which may affect the properties of a functional layer. With this in mind, the current study investigates self-organized arrays formed during the melting of micron-thick Pb films condensed on a tantalum layer.

EXPERIMENTAL

Samples were created by vacuum deposition to a glass plate of the electron beam evaporated Ta and thermally sputtered Pb. The chamber was pumped down to pressure 10^{-7} Torr with a combination of turbomolecular and ion pumps. The thickness of the samples was monitored by the quartz balance method and, further, if necessary, refined by SEM microscopy studies. After deposition, the glass plate was heated to ensure complete melting of the fusible component. As with decreasing film thickness the influence of additional mechanisms of film de-wetting, except for grain boundary de-wetting, increases [16], thick films (6 microns) were chosen for study.

A Tescan Vega 3 LMH scanning electron microscope equipped with a Bruker XFlash 5010 X-ray spectral analysis system were used for surface morphological studies. The obtained images were analyzed with the use of software developed in our laboratory.

RESULTS AND DISCUSSION

Fig. 1 shows the SEM image of the Pb/Ta/glass sample, where the Pb film is completely melted. The traces of thermocapillary motion of melted drops that captured the substance and formed much larger particles appear on the substrate surface (fig. 2). Similar effects were observed in the study [26] during the melting of binary films.

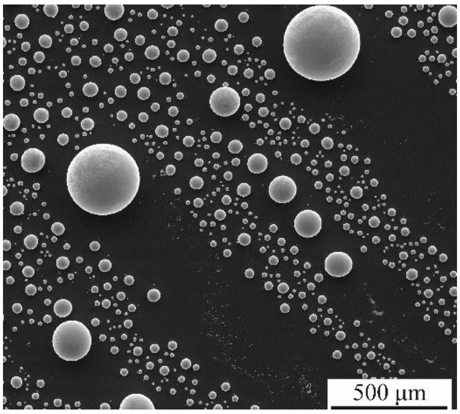

Fig. 1. SEM image of a Pb/Ta film on a glass plate after melting of a fusible component.

Note that, in contrast to [26], in the case of Pb/Ta films, the direction of movement of these droplets appears to be random. This is clearly shown in Fig. 2. Such microstructures may be a result of uneven heating of the film sample. Structurally, the substrate was a glass plate pressed by a metal mask to the massive heater. The edges of the plate have better thermal contact than the central part, which causes a temperature gradient.температури становила близько 5 мК.

This can explain why the detected capillary phenomena appear due to small temperature gradients, the presence of which can significantly change the morphology of the formed structures when heated. Such

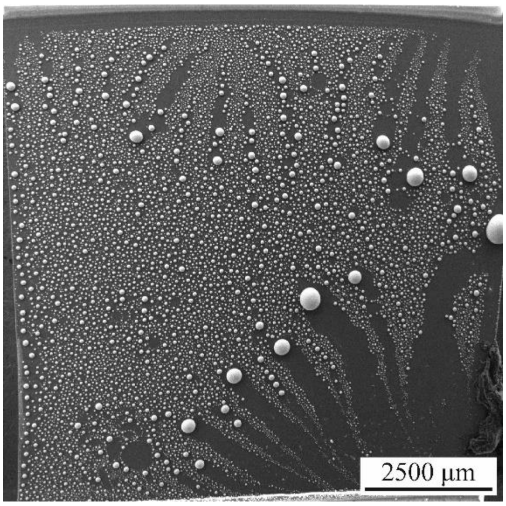

Fig. 2. SEM image of the glass plate with Pb/Ta deposited film obtained after complete melting of Pb.

gradients can occur naturally in many technological processes. Thus, the development of technologies for the creation of self-organizing arrays should take into account such phenomena, reduce their influence, or, conversely, use such capillary motion.

To prove this assumption EDS analysis of the areas with particle motion traces (Fig. 3a) and ordered structure (Fig. 3b) was conducted. In addition to Ta, the presence of Si was detected in obtained spectra. Due to the small thickness of the Ta layer, it was possible to see the spectrum of the glass substrate even at the minimum accelerating voltage. Taking the above into co nsideration, it is possible to estimate the relative thickness of the Ta layer. As seen in spectra (Fig. 3a, 3b), the thickness variation is insignificant and cannot affect the melting substance behavior.

Consequently, the capillary motion of droplets (Fig.1) is caused by random factors and should be considered as an influence of temperature gradients during film de-wetting. This phenomenon should be separated from the matter self-organization processes when structures of regularly shaped spherical particles are formed (Fig.4).

Particle size distribution histograms for an area with an ordered structure of particles were plotted using the method applied in previous studies [16, 18]. The dimensionless size W which is delayed by vertical axis is determined by the formula $W = \frac{4}{3}\frac{\pi N(r) r^3}{S\Delta r}$ and is

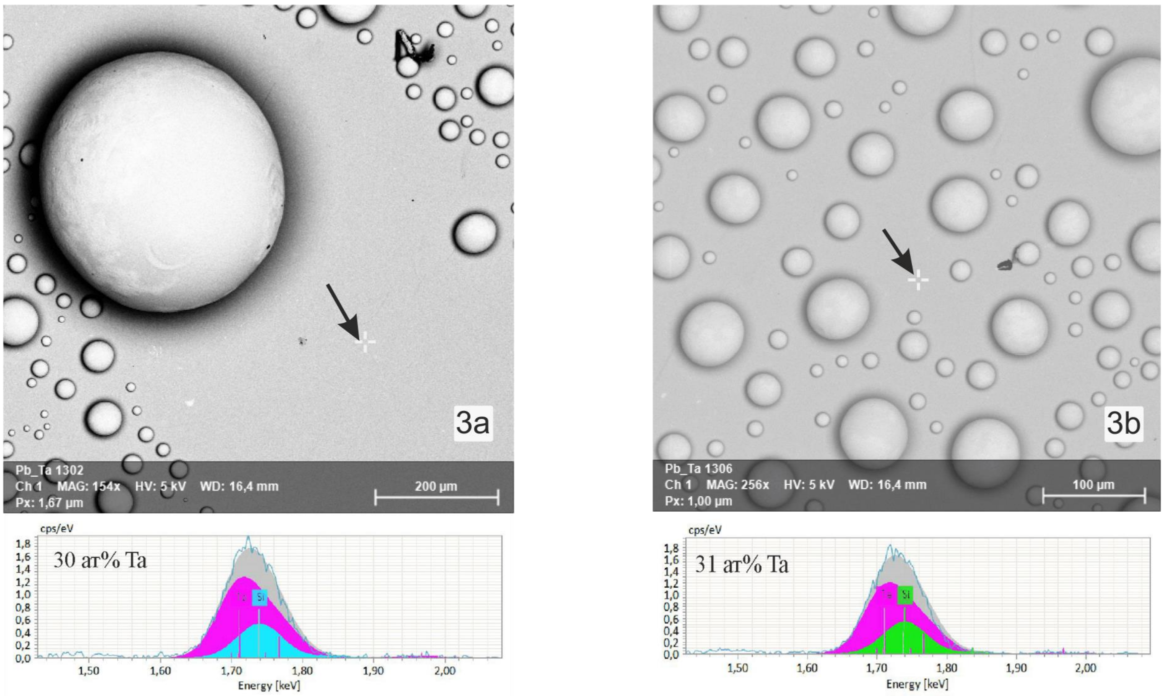

Fig. 3. BSE images of different areas of Pb/Ta film and the corresponding fragments of the EDS spectra. The concentration of Ta, on fig. 3a and fig. 3b, calculated in %, as compared to Si, is a quantitative measure of the thickness of the metallic layer.

An area of the ordered structure particles, similar to those studied previously [16, 18] has been observed together with the areas with molten particle motion traces. We assume that the molten particle motion is a result of the uniformity of the deposited Ta layer.

numerically equal to the mass thickness of the film (in units of Δr), which would form $N(r)$ is particles whose radius (r) get into the interval (r, $r + \Delta r$). Here S is the area of the site on which the histogram is calculated, and Δr is the plotting step.

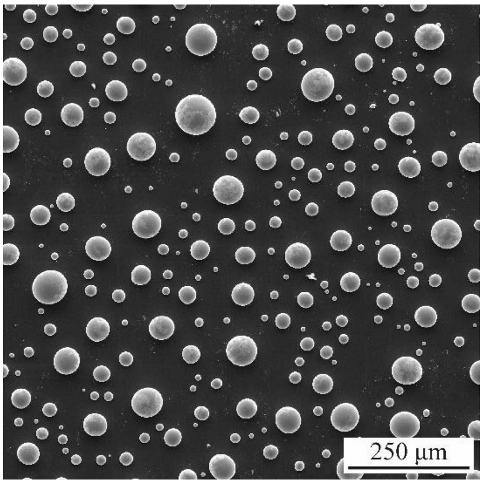

Fig. 4. SEM images of an area of ordered particles Pb/Ta film after thermal treatment.

The shape of the resulting histogram is asymmetric with one maximum (Fig. 5). This is in agreement with the results of [16], which show that the bimodal appearance of the histogram, observed in a narrow interval of mass thicknesses, changes to a unimodal one as the film thickness continues to grow.

The physical reason for de-wettings of a continuous film to islands in the melting process indicates the system tendency to minimize its energy. Energy gain of the de-wetted film may be evaluated using coverage of the film on a substrate or using the most probable radius of the formed particles. Taking into account that the substrate coverage is 0.2 and the most probable radius of the formed particles is 30 μm, the energy gain can be estimated as 370 mJ/m2.

The density of particles on the substrate is an important characteristic of the sample, which provides information about the evolution mechanisms of the film morphology during the formation of the surface structure. The determination of the particle density, the smallest particles are excluded from calculations. The following criterion is used: all particles in the image are sorted out by size and only the first N particles that contain 90% mass of the layer, are taken for calculations. Such particles affect the main properties of functional structures and are easy to observe. It was observed that Pb film on the Ta layer had a density of 300 particles per mm^2. This value is noticeably smaller in comparison with the particles density for lead deposited on carbon [16]. This indicates a decisive role of the tantalum layer in the formation of the studied structures. It appears that despite poor wetting by Pb, a layer of Ta simplifies the particles motion. This facilitates coalescence, which is present both in the region of capillary motion (Figs. 1, 2) and in the areas of the substrate where ordered structures were observed. Taking into consideration all the above, we can conclude that the asymmetry of the obtained distribution histogram is natural and can be explained by the presence of the two types of particles in the heat-treated sample. Primary particles are formed by grain-boundary dispersion and secondary particles are formed by coalescence of primary particles.

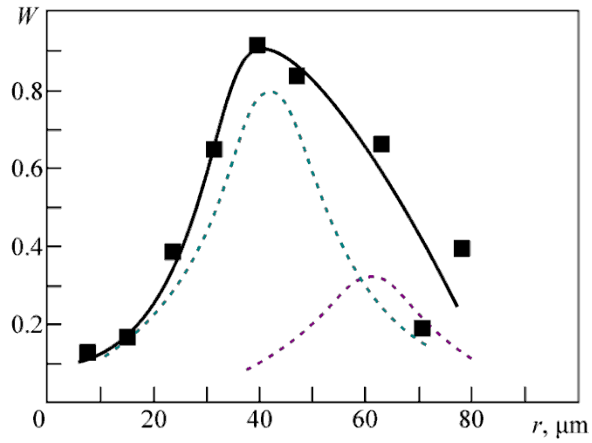

Fig. 5. Histogram of the size distribution of particles formed during the melting of a continuous film of Pb on the Ta surface.

ACKNOWLEDGMENT

This project has received funding through the MSCA4Ukraine project, which is funded by the European Union and was supported by the Ministry of Education and Science of Ukraine

CONCLUSIONS

1. This study shows that the Pb films of micron thickness, deposited on thin layers of Ti, form arrays of spherical particles after melting.
2. The shape of the particles indicated the poor wetting in the system.
3. The histogram of distribution by the size of Pb particles is single-modal but has signs of asymmetry. Asymmetry may indicate that the microstructure of the studied samples is formed by the two mechanisms. The first mechanism is the thermal decay of the initial solid films, occurred on the boundaries of grains of the polycrystalline film. As a result, primary type particles are formed. The second mechanism is the coalescence of such primary particles, due to which particles of a different size type appear.

CONFLICT OF INTEREST

The authors report no conflict of interest.

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МОРФОЛОГІЧНА СТРУКТУРА ОСТРІВЦЕВИХ ПЛІВОК СВИНЦЮ, РОЗПЛАВЛЕНИХ НА ПОВЕРХНІ ТАНТАЛУ.

І.Г. Чурілов, О.О. Невгасимов, С.І. Петрушенко, С.В. Дукаров, В.М. Сухов

Харківський національний університет імені В.Н. Каразіна, майдан Свободи, 4, 61022 Харків, Україна
E-mail: igor.churilov@karazin.ua

Надійшла до редакції 05 квітня 2023 р. Переглянуто 11 травня 2023 р.
Прийнято до друку 17 травня 2023 р.

Плавлення тонких шарів речовини, що знаходиться на погано змочуваній поверхні, розглядається як ефективний спосіб створення самовпорядкованих масивів металевих частинок. Такі масиви здатні як покращувати технологічні властивості функціональних структур, так і самі виступати функціональним елементом сучасних приладів та систем.

Під час плавлення твердого шару на погано змочуваній підкладці утворюється масив частинок сферичної форми, що рівномірно розподілені поверхнею підкладки. Розподіл за розмірами острівців, що утворюються після плавлення суцільних плівок, осаджених за механізмом пара-кристал, визначається насамперед початковими етапами їх диспергування, за яких достатньо тонка суцільна плівка розпадається ще у твердому стані.

Робота присвячена дослідженню процесів самовпорядкування, які відбуваються під час плавлення плівок свинцю, що були осаджені на танталову підкладку. Плівки конденсували на скляні пластини, у високому вакуумі після чого нагрівали до температури, що дещо перевищує температури плавлення свинцю. По завершенню термічного впливу зразки діставали з вакуумної камери та досліджували з використанням SEM мікроскопії та EDS аналізу.

Встановлено, що під час плавлення плівок свинцю мікронної товщини утворюються масиви частинок сферичної форми. Гістограми розподілу за розмірами таких частинок є досить широкими та можуть бути представлені як бімодальні з максимумами, що частково перекриваються. Це можна пояснити активними процесами коалесценції у зразках великої товщини. Показано, що незначні температурні градієнти можуть викликати помітні кінетичні ефекти, завдяки яким окремі частинки пересуваються на макроскопічні відстані та захоплюють оточуючу речовину. Оцінено енергію, яка пов'язана з оптимізацією морфологічної структури вакуумного конденсату та є фізичним чинником диспергування.

Ключові слова: *диспергування, самовпорядкування, острівцеві плівки, плавлення, масиви частинок, розподіл за розмірами.*